VITREOUS RADIOELECTRETS: MATERIALS FOR SHIELDING SPACECRAFT AGAINST RADIATION (REVIEW)

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Using the EPR method, it was established that the main centers of negative charge accumulation are electroactive phosphor-oxygen ion radical PO_3^{2-} of the electron type. The majority of the considered phosphate glasses are capable of accumulating such a charge. However, the most effective one among the alkaline-earth modifiers is magnesium. The results obtained make it possible to develop with a great degree of reliability the compositions and technology of inorganic glasses with a prescribed set of service properties.

It is known [1, 2] that protective glass coatings intended to reduce the ionization-radiation effect are installed on the surface of semiconductor photoelectric converters (PC) of the solar batteries on a spacecraft (SC). To ensure the maximum efficiency in converting solar energy to electrical energy, the radiation-shielding properties of the glass plates should be combined with high parameters of optical transparency and heat-reflecting properties. Furthermore, severe limitations of the weight parameters of the coatings encourage the search for the optimum solutions, enabling one to diminish the space radiation effect on the PC while preserving or, if possible, decreasing the coating thickness.

Based on the recommendations given in [3, 4], the authors in [5] proposed using dielectric materials capable of accumulating a volume charge (VC) under electron irradiation, while orbiting in the Earth's radiation belt, i.e., materials with radioelectret properties. In this way, one can implement a new approach to the improvement of coating properties, which is based on a combination of the traditional passive shielding method employing a certain material and the active-protection method, in which the electron-electric fields of the VC are used for deceleration and deviation. Such a possibility in principle follows from the results of the experimental studies in [6, 7], which established that the VC formation under irradiation in an accelerator generates intense internal fields in some high-ohm dielectrics, which are sufficient to exert additional deceleration and deviation of electron beams in the dielectric layer. It was suggested that such a mechanism could be used to accomplish a significant increase in the service life of SC solar batteries orbiting the radiation belt of the Earth.

Vitreous inorganic materials were developed to investigate the possibility of implementing this principle in radiation shielding of SC. Inorganic glasses are preferable to charging polymer materials because of their higher heat resistance and hardness, as well as initial high optical transparency.

The interaction of fast electron beams with samples of alkali-free aluminophosphate glasses was studied in [7] for the purpose of establishing the effect of the physicochemical properties of inorganic glasses on their capacity for forming intense internal electric fields under electron irradiation in an accelerator. It was established that the VC electric fields arising in the tested glass samples were sufficient for additional reflection and deceleration of electron beams. In this case, the field effect was not only observed during irradiation but persisted in some glass compositions after a long time lapse and was registered in repeated testing. The estimated intensity of electric fields reached 0.4 – 2.0 MV/cm, depending on the atomic number and the concentration of the modifier element contained in the glass [7, 8].

The studies in [8 – 10] researching the effect of improvement of radiation-shielding properties of alkali-free aluminophosphate glasses after electron charging in an electron accelerator demonstrated that for relatively thin glass layers (when their thickness d did not exceed half of the electron ionization path R), the additional decrease in the absorbed dose rate caused by the field is not great. The most perceptible decrease in the dose rate P was registered beyond the glass samples of thickness $0.5R < d < 0.8R$, and was equal to 75 – 95% of the dose rate in the absence of electric fields. As the field intensity increases, the shielding effect of the charged dielectric layer becomes more perceptible and can decrease the absorbed dose to one-tenth.

The testing of the shielding effect produced by volume radiation charging of glass coatings was also carried out on the surface of a returnable Earth satellite in containers for re-

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TABLE 1

Glass	Molar content, %*						Relative intensity of EPR signals of phosphor-oxygen radicals			Relative change in intensity of doublet ion radical PO_3 after sample fracture
	P_2O_5	La_2O_3	B_2O_3	Al_2O_3	MgO	CaO	center I	center II	center III	
1	51.2	9.2	8.9	6.1	24.4	–	0.95	1.05	–	0.74
2	54.8	9.9	9.5	6.5	–	19.0	1.00	1.05	–	0.80
3	60.0	10.9	10.4	7.2	–	–	1.15	1.90	–	0.84
4	50.0	–	5.0	–	45.0	–	0.69	0.90	0.50	0.75
5	50.0	–	–	5.0	45.0	–	1.90	1.23	–	0.55
6	75.0	–	–	25.0	–	–	1.70	0.65	0.30	0.50
7	70.0	–	–	30.0	–	–	0.90	0.90	1.00	0.80
8	50.0	–	–	–	–	–	1.00	1.00	1.00	0.85
9	50.0	–	–	–	50.0	–	1.70	0.70	–	0.98
10	64.8	1.1	10.1	9.25	14.7	–	1.26	1.15	0.40	0.77
11	60.0	–	3.0	10.0	12.0	10.0	1.40	1.07	–	0.40
12	75.0	25.0	–	–	–	–	0.30	2.35	0.16	0.88

* Glass 3 contain 11.3% SrO, glass 8 contain 50.0% BaO, glass 11 contain 5.0% ZnO.

search equipment [8]. The attenuation of the space-radiation dose behind 0.5-mm-thick glass plates, which had been previously charged on the Earth, was investigated. The volume charge in the glass plates was created by electron irradiation in a linear accelerator two weeks before installing the plates in the satellite. The electron beam energy was 0.9 MeV, and the average current density was 0.01 $\mu A/cm^2$.

The improved shielding properties acquired under these conditions were manifested in the fact that the dose rate behind the glass sample at the end of irradiation decreased to a persistent minimum value constituting 0.7 of the initial dose rate, which was equal to 20 cGr/sec.

The experiment on the satellite surface established that thin phosphate glass plates precharged on the Earth (the glass thickness was similar to that of the protective coating on solar batteries) diminish the radiation absorbed dose at the orbit of the Kosmos satellite by a factor of 1.5 – 1.8, i.e., exhibit additional protective properties.

The experiments in accelerators and satellites were performed on alkali-free aluminophosphate glasses with a high molar content of P_2O_5 (51 – 70%) with a B_2O_3 content of 9 – 13% and an Al_2O_3 content of 6 – 10%. Furthermore, the La_2O_3 content varied within a wide range (from 0.5 to 14%), and alkaline-earth oxides (MgO, CaO, SrO, and BaO) were added in different quantities (from 1% to 25%). The optimum compositions of aluminophosphate glasses with respect to the values and stability of internal electric fields related to the accumulation of the volume charge were empirically determined in [7 – 10]. However, up to now the microscopic nature of the origin and accumulation of the VC in glasses, as well as the role of individual glass components in the charge accumulation efficiency, have not been sufficiently studied. The solution of the problem of effective shielding of spacecraft battery cells is closely related to developing glass compositions needed to make optical coatings for semiconductor PC for spacecraft solar batteries (RF Patent No. 2144718) [11].

The present paper attempts an analysis at the microscopic level of the origin and the conditions for the formation of electron-trapping centers in oxide glasses, whose compositions varied within wide ranges, including glasses tested in authentic conditions of open space.

The compositions of the investigated glasses are given in Table 1.

Experimental glass samples were melted in 100-g corundum or quartz crucibles in a laboratory electric furnace with silite heaters in a neutral atmosphere. The melting temperature was 1350 – 1500°C with an exposure duration of 0.5 – 2 h. The melted glass was cast onto a preheated metal substrate. The annealing temperature was 520 – 570°C. The glass samples were machine-treated: ground and polished to the required dimensions.

The studies in [12, 13] using the electron paramagnetic resonance (EPR) effect demonstrated that radicals PO_4^{2-} and PO_3^{2-} formed under the effect of electron or γ-radiation can act as electron trapping centers in phosphate glasses. The present study considered the EPR spectra in glass samples irradiated with electrons in an accelerator (electron energy 1 MeV, current density 0.01 $\mu A/cm^2$, exposure 10 min), with the aim of finding out whether the known ion radicals are centers for the accumulation of excessive volume charge.

First, the EPR spectra were measured in electron-irradiated (charged) monolithic samples with a known weight (from 0.09 to 0.17 g). Next, the samples were fractured by mechanical impact into several smaller fragments. It was assumed that mechanical destruction of the charged samples would cause discharging of excessive VC, similar to the phenomenon described, for example, in [14]. It should be noted that the obtained fragments were not small enough to lead to the formation of paramagnetic centers caused by breaking of chemical bonds. Next, the EPR spectra were recorded under the same instrumental parameters as the EPR spectra of the respective monolithic samples.

The EPR were measured with a modified RÉ-1306 radiospectrometer of 3-cm range at room temperature and at the temperature of liquid nitrogen.

ERP spectra in γ- and electron-irradiated phosphate glasses. The formation of phosphor-acid ion radicals under the effect of γ-irradiation was discussed in numerous papers, starting with [15], in which the EPR method was used for these studies. Phosphate glasses are known to have the EPR spectra of different phosphor-acid ion radicals containing one or several phosphor atoms. The radicals with one phosphor atom exhibit doublet splitting caused by superfine interaction of the non-coupled electron with the magnet nucleus ^{31}P having spin $I = 1/2$. At present, six types of doublets are known for phosphate glasses, which are characterized by different types of splitting. Three of these types were registered in the glasses considered.

The ion radical PO_4^{2-} (center I) is usually considered as a hole captured by the non-bridge oxygen ion; its superfine structure (SFS) constant is equal to $35 - 45$ Oe. With an increasing number of non-bridge oxygen atoms in the phosphor-oxygen tetrahedron, an increase is observed in the intensity of the EPR signal [15].

The ion radical PO_3^{2-} correlates with two types of centers, which are characterized, respectively, by SFS constants of about $750 - 950$ Oe (center II) and about $1200 - 1300$ Oe (center III). This is a four-atom radical, in which the uncoupled electron is localized on the central phosphor atom. Both centers have a similar nature, but they are formed on different structural elements of phosphate glasses.

It is demonstrated in [16] that the introduction of Ce^{3+} additive to phosphate glasses does not alter the intensity of the PO_3^{2-} signals, which shows that these radicals are formed as a consequence of electron capture by phosphor. It is assumed that center II in radical PO_3^{2-} is an electron trapped in the vacancy of the non-bridge oxygen atom. Starodubtsev et al. [13] regard center II as an electroactive center of the vacancy type.

Figure 1 shows the EPR spectrum of monolithic glass 7 irradiated with electrons. The spectrum contains three types of doublets generated by phosphor-oxygen radicals. The peak intensity of one of the lines in each doublet in the spectrum of sample 7 was taken as the measurement unit. Since the shape and the width of lines in each doublet virtually did not vary from one glass sample to another of the same chemical composition, their relative peak intensity can be the measure of variation in the concentration of a certain type of radical from one sample to another. Furthermore, the relative peak intensity was scaled to the sample weight unit. It should be stressed that a specific peak intensity unit was selected for each doublet (it is seen in Fig. 1 that they are different).

It follows from Table 1 that center I is found in all glasses. Center I is related to the optical absorption band with the maximum at 560 nm, which is responsible for the crimson color of the samples. According to the data in [13], the
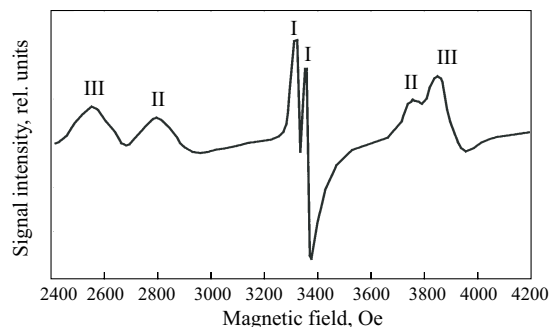

Fig. 1. EPR spectrum of glass 7 illustrating doublet signals I, II, and III for three typical phosphor-oxygen radicals, whose parameters are given in Table 1.

intensity of signal I for γ-irradiated glasses increases with an increasing number of non-bridge oxygen atoms. The same regularity is observed in electron irradiation. Thus, the highest intensity of signal I among all considered glasses is observed in glasses of the metaphosphate composition (4, 5, 8, and 9). It is established in [12] that the intensity of signal I increases under an equimolar replacement of a cation with lower electronegativity with a cation with higher electronegativity. A growth in the intensity of this signal from magnesium toward barium, i.e., with increasing electronegativity of the alkaline-earth element, was observed in the considered electron-irradiated glasses, and the intensity of signal I in all samples containing over 50% P_2O_5 was lower than in metaphosphate glasses, especially in the case of glass 12.

Center III, according to the data in [15], is localized in the branching points of the phosphate chains, and its EPR spectrum under γ-irradiation is observed only in ultraphosphate glasses (i.e., with the molar content of P_2O_5 over 50%). This spectrum is also observed in the case of electron irradiation (samples 6 and 7). However, whereas the specified signal has high intensity in lanthanum-bearing γ-irradiated glasses [15], after electron irradiation the signal is very weak (sample 12) or is not observed at all (sample $1 - 3$). It should be noted that doublet IV was identified in the spectrum of glass 12. Such results can be expected based on the data for highly polymerized γ-irradiated glasses.

As for the behavior of the ion radical PO_3^{2-} (center II), the intensity of the signal from center II in gamma-irradiated phosphate glasses correlates with the intensity of doublet I [15]. Under electron irradiation, these signals change in the opposite direction. It should be noted that this result is not unexpected, as it had been shown in [17] that the formation of hole centers under electron irradiation impedes the accumulation of electrons in electron traps, which leads to the formation of center I. Thus, whereas the behavior of radical I in electron-irradiated phosphate glasses is similar to its behavior under γ-irradiation, the behavior of center II and partly of center III differs significantly. Starodubtsev et al. [12, 13] relate the VC accumulation in phosphate glasses precisely to center II.
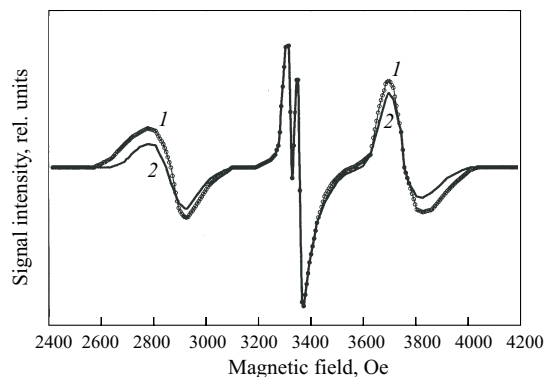
Fig. 2. EPR spectra of glass 2: *1*) in a monolithic glass sample; *2*) after mechanical fracture of the sample.

The study in [13] additionally investigated phosphate glasses subjected to long-term storage after irradiation with electrons having an energy of 1.2 MeV, as well as samples irradiated with electrons with an energy of 150 keV in the sample pulse mode as in [12], with specially selected temperatures, which makes it possible to satisfy the conditions under which only center II is formed. Thermally stimulated electron emission was studied, and it was demonstrated that the most intense emission related to the liberation of electrons from traps coincides with the thermal stability boundary of centers II and with the region of the highest decline rate of the electric field. As a result, it was concluded that centers II, which are tail-type PO_3^{2-} radicals, are the centers of electron accumulation.

EPR spectra in phosphate glasses irradiated by high-energy electrons after mechanical destruction of glass. Figure 2 shows the EPR spectra of glass 2 before and after fracture. The spectrum of this sample after electron irradiation contains two doublets of centers I and II. It can be seen that spectrum I (Fig. 2, central part) is not changed after the sample fracture (the two doublets from the two samples merge into one), whereas the intensity of both components of doublet II decreases by 20 – 25%. Table 1 indicates the coefficients constituting the ratio of doublet II intensity after the sample destruction to the intensity before the fracture. As can be seen in the data of Table 1, these parameters in most phosphate glasses amount to 0.85 ± 0.05, which correlates with a 15 – 20% decrease in intensity. The exceptions are glasses 4, 5, and 9, in which this value reaches 50 – 60%, i.e., under mechanical destruction of samples, the electron centers of type II lose about 50% of their electrons. At the same time, the electrons in sample 8 are virtually not lost in the fracture.

Analyzing the composition of samples with the highest electron loss, one can see that the molar content of MgO in them is 45 – 50%. Furthermore, the relative variation in the doublet intensity in samples 1, 10, and 11 indicates that the electron loss in them under glass fracture constitutes 23 – 26%. The MgO content in them is 12 – 25% (Table 1).

Mechanism of electric charge accumulation in phosphate glasses. Under mechanical destruction of glass, the number of electron-type radicals PO_3^{2-} (center II) decreases. Based on this fact, as well as on published data [12, 13, 17], it can be inferred that the electrons traps responsible for the formation of these radicals under ionization radiation are also the centers for capture and accumulation of the excessive volume charge under irradiation of glass with electrons. Contributions to this center are made by both the radicals formed in the capture of secondary ions related to ionizing radiation and the electrons injected in the course of electron irradiation.

It should be noted that most phosphate glasses appear to be able to accumulate electric charge, since they contain electrically active centers capable of capturing electrons. A more significant feature is their capacity not only for capture but also for long-term storage of electrons. The most effective in this respect are magnesium-containing glasses that lose up to 50% of electrons from traps under a mechanical impact against glass, whereas other glasses lose on the average less than 20%. The studies in [7, 8] include calculations of the intensity of the electric field of VC typical of various glasses (E, $MV \cdot cm^{-1}$), as well as accumulated energy density (W, $J \cdot cm^{-3}$), Thus, for glass 10, $E = 2.1$ and $W = 0.75$, whereas for glass 3, $E = 0.96$ and $W = 0.25$. A comparison with the data in Table 1 indicates that E and W are higher in glass 10, which exhibits a greater decrease in the EPR signal of center II under destruction. Moreover, as shown in [7], which describes the results of an experimental study of the electrophysical properties of alkaline-free aluminophosphate glasses interacting with electron beams, under the equi-weight replacement $MgO \rightarrow CaO \rightarrow SrO$, the specific resistance in glasses 1 – 3 decreases to one-third, and the dielectric constant increases 1.25 times. Both factors play an important role in the accumulation of the volume charge. It follows from the data in Table 1 that the doublet intensity increases in the same direction. At the same time, sample 8, in which center II after the glass fracture is changed least of all, contains only BaO as a modifier.

The study in [15], which also registered a decrease in electric charge accumulation in aluminophosphate glasses directed from magnesium to barium, attributes this effect to the fact that the Ba–O bond is stronger than the Mg–O bond, due to the greater difference in electronegativity of the elements in the first case, which contributes to a more intense transfer of electron density from the modifier to phosphor and reduces its capacity for electron trapping.

This concept also agrees with the modification of the composition at the expense of other elements. Thus, a replacement of 50% magnesium (electronegativity $\chi = 1.23$) with 50% barium ($\chi = 0.97$) leads to a significant increase in the doublet intensity (from 0.40 to 0.98 in glasses 8 and 9, Table 1). A replacement of 5% magnesium with aluminum ($\chi = 1.5$) or boron ($\chi = 2$) also causes an increase in the doublet intensity up to 0.50 and 0.55, respectively.

Thus, using the EPR effect, it was established that the main centers of negative charge accumulation are electro-

active phosphor-oxygen ion radicals PO_3^{2-} of the electron type. The majority of the considered phosphate glasses are capable of electric charge accumulation. However, magnesium is the most effective of all alkaline-earth modifiers. The results obtained make it possible to design with a great degree of accuracy compositions and production technologies of inorganic glasses with a prescribed set of service properties.

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